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(54) **Vegetable oil derivatives as lubricant additives.**

(57) There is disclosed lubricant additives that comprise a combination of vegetable oil as a triglyceride or a wax ester, sulfurized triglyceride vegetable oil or sulfurized wax ester of vegetable oil, and phosphite adducts of triglyceride vegetable oil, wax ester of vegetable oil or jojoba oil. There is also disclosed a process for sulfurizing triglyceride vegetable oil that is soluble in a lubricant base, such as mineral oil.

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VEGETABLE OIL DERIVATIVES AS LUBRICANT ADDITIVES

TECHNICAL FIELD

The present invention relates to lubricant compositions and lubricant additives and to methods for producing lubricant additives with antifriction properties that contain vegetable oil and vegetable oil derivatives as lubricating agents. More specifically, this invention relates to wax esters of vegetable oil fatty acids, sulfurized vegetable oil triglycerides, sulfurized vegetable oil wax esters, vegetable oil triglycerides, phosphite adducts of vegetable oil triglycerides, and phosphite adducts of vegetable oil wax esters as lubricant additives in various combinations, and from various vegetable oil sources.

BACKGROUND OF THE INVENTION

Lubricants are widely used to reduce the friction between the surfaces of moving parts and thereby reduce the wear and prevent damage to the parts. Most lubricants are comprised principally of a base stock which is generally a relatively high molecular weight hydrocarbon. In applications where the amount of pressure applied to the moving part is quite high, lubricants which are comprised of only hydrocarbon base stock tend to fail and the contacting parts are damaged. It is well known to add materials (lubricant additives) to increase the high pressure performance of lubricants. These materials are generally called "extreme pressure additives." Examples of extreme pressure additives are sulfurized materials such as sulfurized sperm whale oil or sulfurized jojoba oil.

Wax esters can be sulfurized from natural wax esters, such as from jojoba oil, and from synthesized wax esters, such as from vegetable oil triglycerides and liberated fatty acids. Natural wax esters have produced formulated sulfurized products that provide effective lubricant additive compositions. However, the problems with the natural wax esters are availability and cost. The vegetable oils have to be transesterified from the free fatty acids to produce the wax esters. For practical applications, however, the vegetable oil triglycerides have the disadvantage that cost-adding conversion steps are necessary to form a wax ester for sulfurization, rather than a direct sulfurization of the triglyceride. These extra processing steps make vegetable oil wax esters relatively uneconomical as lubricant additives.

Princen et al., "Development of New Crops for Industrial Raw Materials," J. Amer. Oil Chemists Soc., 61: 281-89, 1984, tried to sulfurize meadowfoam oil by sulfurizing the wax esters of the meadowfoam fatty acids. Princen et al. found that sulfurization of the unaltered triglyceride oil can react with sulfur under traditional sulfurization conditions to yield factice, a solid chemical rubber and an unacceptable lubricant additive. Factice forms due to cross-linking of hydrocarbon chains by polysulfide bonds to create an insoluble material. The first sulfurized wax ester of meadowfoam oil preparation in Princen et al. had good lubrication properties, but it corroded copper, foamed excessively, and thickened excessively under in-use conditions in a hot gear box. The second sulfurized wax ester of meadowfoam oil preparation in Princen et al. was made with different synthesis conditions, but the second preparation decreased copper corrosion and maintained lubricating properties but produced more foam and did not meet a thermal stability test. The third preparation in Princen et al. used wax esters from enriched monoene and diene acids. The diene wax ester (made from monoenoic fatty acids) resulted in increased wear scar but favorable other properties.

Wakim, United States Patent No. 3,986,966, after demonstrating that sulfurization of triglycerides alone gave resinous products mostly insoluble in base oils, added nonwax methyl esters of a fatty acid of 18 to 22 carbon atoms which are monounsaturated to improve the solubility of the sulfurized triglycerides.

Hutchinson et al., United States Patent No. 3,740,333 refers to sulfurized blends of lard oil and a saturated wax ester, the essential element of the wax ester being derived from a C₁₀₋₁₆ saturated alcohol and a C₁₈₋₂₂ unsaturated acid.

Kammann et al., "Sulfurized Vegetable Oil Products as Lubricant Additives," J. Amer. Oil Chemists Soc., 62:917-23, 1985, found that sulfurized vegetable triglyceride oils resulted in rubbery products, in some cases even at a 12% sulfur content. Kammann et al. tried using sulfurization with large amounts of methyl lardate, but obtained factice or near factice with meadowfoam oil. Kammann et al. was able to sulfurize only by adding 10% unsaturated oleic acid before sulfurization; however, the resulting product properties were undesirable as a lubricant additive.

There are many problems using a sulfurized vegetable oil and extra expenses making a wax ester from a triglyceride vegetable oil. Therefore, there exists a need in the art to find lubricant additive compositions that can use the relatively abundant supplies of vegetable oils without resorting to the multiple processing

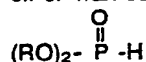
steps of making wax esters of the fatty acids. There further exists a need in the art to be able to sulfurize triglyceride vegetable oils for use as lubricant additives.

5 SUMMARY OF THE INVENTION

Briefly stated, the present invention encompasses lubricant additives comprising combinations of triglyceride vegetable oil with at least one of a sulfurized vegetable oil and a phosphite adduct of vegetable oil. The vegetable oil is a triglyceride in its native state with the fatty acids having from about 16 to about 26 carbon atoms and at least one double bond, but no more than three double bonds for at least 90% of the fatty acids. Preferably, the vegetable oil fatty acids are C₁₈₋₂₂ with the majority of fatty acids having one double bond. Most preferably, the vegetable oil is meadowfoam oil, rapeseed oil or crambe oil.

The vegetable oil can be in the form of the native triglyceride or as a mixture with vegetable oil wax ester. The sulfurized vegetable oil comprises either a sulfurized mixture of the triglyceride form of the vegetable oil with from about 25% to about 75% of a wax ester or sulfurized vegetable oil wax ester. The wax ester for mixing with the triglyceride vegetable oil for sulfurization is jojoba oil or is derived from a C₁₈₋₂₂ unsaturated fatty acid and a C₁₈₋₂₂ unsaturated fatty alcohol. Preferably, the wax ester is a naturally occurring wax ester, such as jojoba oil, or the wax ester of meadowfoam oil or rapeseed oil. The phosphite adduct of the vegetable oil can be a mono- through hexa-adduct of the triglyceride form of the vegetable oil, or a mono- through tetra-adduct of the wax ester form of the vegetable oil.

The phosphite adduct of the vegetable oil is formed by the reaction of the native triglyceride vegetable oil or wax ester of the vegetable oil and a compound of the formula:



wherein R is H, C₁₋₁₂ alkyl, C₁₋₁₂ aryl, C₁₋₁₂ alkaryl, C₁₋₁₂ aralkyl, and cyclo C₄₋₁₂ alkyl. Preferably, R is C₄₋₈ alkyl, C₄₋₈ alkaryl, C₄₋₈ aralkyl, or cyclo C₄₋₈ alkyl. Most preferably, R is n-butyl.

The present invention further comprises a lubricating composition consisting essentially of a lubricant base and a lubricant additive wherein the lubricant additive comprises a mixture of at least two ingredients from different classes of ingredients selected from the group consisting of three classes of ingredients: wherein the first class of ingredients comprises a triglyceride vegetable oil, a wax ester of the vegetable oil, and a combination thereof; wherein the second class of ingredients comprises: a sulfurized vegetable oil wax ester; a sulfurized triglyceride vegetable oil within the range of from about 25% to about 75% vegetable oil, and from about 25% to about 75% of a wax ester, as described herein; and a combination thereof; and wherein the third class of ingredients comprises a phosphite adduct of triglyceride vegetable oil, a phosphite adduct of the vegetable oil wax ester, and a combination thereof.

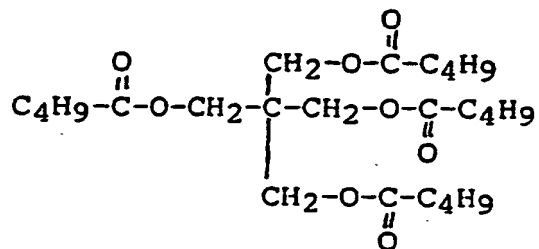
DETAILED DESCRIPTION OF THE INVENTION

The present invention is a lubricant with anti-friction properties, including antiwear and load-carrying properties, and comprising a lubricant base and a lubricating additive. The lubricant base stock can be selected from a large class of compounds. Most often the base is a high molecular weight hydrocarbon. The lubricant base is, preferably, a mineral oil, although synthetic hydrocarbon lubricating oils and other synthetic lubricating oils, such as ester lubricating oils and mixtures thereof (e.g., mixtures of mineral and synthetic lubricating oils), can also be used, provided that the desired proportion of lubricating additive is soluble in the lubricant base. The mineral oils include HVI (high viscosity index) oils, Bright Stock, and Bright Stock extract as well as MVI and LVI oils. The viscosity index of these oils can vary from -150 to 150. The 210° F viscosities of these oils can vary from 2 to 140 centistokes. Mixtures of these oils are also suitably employed.

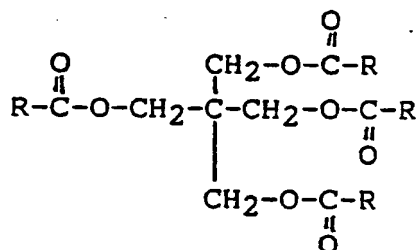
Examples of lubricant bases include hydrocarbon oil; synthetic hydrocarbon; an ester-based lubricant; a mineral oil; a mixture of a mineral oil and an ester-based lubricant; a mixture of mineral oil, synthetic hydrocarbon, and an ester-based lubricant; a mineral oil-based grease; and a synthetic hydrocarbon-based grease. Specifically, the base fluids are:

- a. mineral oils, such as paraffinic neutral 100", furtural-refined paraffinic oil, solvent-refined naphthenic oil, and solvent-refined aromatic oil;
- b. synthetic hydrocarbon oils, such as hydrogenated or partially hydrogenated polydecene and other olefins, hydrogenated hexene oligomer, hydrogenated octene oligomer, hydrogenated decene oligomer,

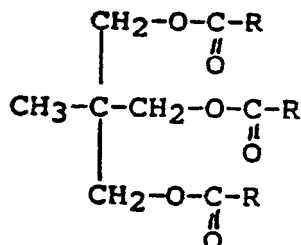
hydrogenated C₆-₁₀ oligomer, and hydrogenated C₈-₁₀ oligomer;
 c. ester fluids, such as pentaerythritol esters having the structures:



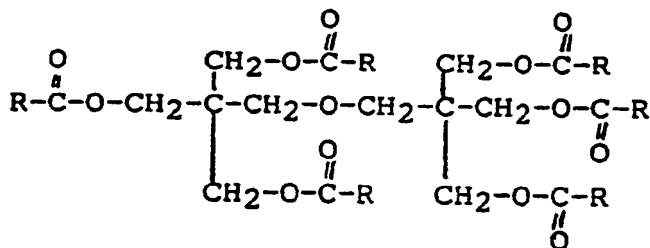
and



wherein R is C₄H₉, C₆H₁₃, C₈H₁₇, or mixtures thereof; esters of trimethylolpropane and dipentaerythritol of the structures:



and



wherein R is defined as above;

di-2-ethylhexyladipate; di-2-ethylhexylsebacate; didecyladipate; and didecylsebacate;

d. dialkylbenzenes, such as didodecylbenzene;

e. polyglycols, such as UCON fluids, polypropylene glycols of 1000 to 3000 molecular weight and polyethylene glycols of 1000 to 3000 molecular weight;

f. alkylaromatics; and

g. dicarboxylic acids.

The lubricating additives of the present invention can be used with a variety of lubricating compositions, such as cutting fluids, precoat oils, metal-working oils, ATFs (automatic transmission fluids), gear oils, way lubricants, greases, aviation oils, textile lubricants, hydraulic oils, circulating oils, steam cylinder oils, spindle oils, fire-resistant fluids, and automotive and marine oils.

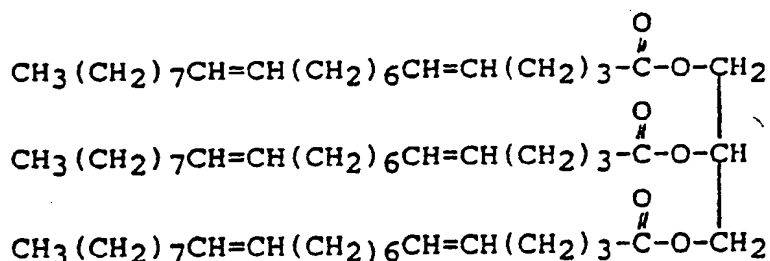
Vegetable oils useful for the present invention are a tri-ester of three long chain unsaturated fatty acids with glycerol, a tri-hydroxy alcohol. Jojoba oil, by contrast, is a monoester of a long chain unsaturated acid and a long chain unsaturated alcohol. The fatty acids are from about 16 to about 26 carbon atoms in length and are at least monounsaturated and not more than triunsaturated for at least 90% of the vegetable fatty acids. Preferably, the vegetable oil fatty acids are C_{18-22} with the majority of fatty acids being monounsaturated. Most preferably, the vegetable oil is meadowfoam oil, rapeseed oil or crambe oil. Other useful vegetable oils include: soya bean oil, peanut oil, safflower oil, sunflower seed oil, cottonseed oil, olive oil, corn oil, coconut oil, palm oil and the like.

Meadowfoam (*Limnanthes laba*) is a herbaceous winter annual plant native to the Pacific Northwest region of the United States. The common name "meadowfoam" was given because of the appearance of its solid canopy of creamy white flowers at full bloom. Meadowfoam is currently being grown commercially in Oregon's Willamette Valley.

Meadowfoam oil is extracted from meadowfoam seeds. Meadowfoam seeds are pear-shaped, consisting of a thin, brown, striated hull surrounding a relatively soft, light-colored dicotyledon kernel. The seeds, measuring about 2 x 3 mm, average about 150 to the gram. The kernels contribute about two-thirds of the total weight and contain essentially all of the triglyceride oil. Commercial meadowfoam seeds generally contain about 27% oil.

Meadowfoam oil is a triglyceride with approximately 95% of the fatty acids being C_{20} and C_{22} fatty acids and primarily monoenoic (single unsaturation). Further, there is a lack of conjugation of even the dienoic fatty acids, as the double bonds are located far from each other. This amount of unsaturation provides for greater oxidative stability than is found in conjugated, unsaturated fatty acids. Meadowfoam oil triglyceride has the α - and α' -positions usually occupied by 5' monoenoic acids and the major fatty acids are: 5-eicosenoic, 11-eicosenoic, 5-docosenoic, 13-docosenoic, and 5,13-docosadienoic acids.

Meadowfoam oil, for example, contains about 20% diene in the acid portion of the molecule. An example of this diene structure is 5,13-docosadienoate ester of glycerol:



The diene structure is believed to be the major cause for problems in the art sulfurizing meadowfoam oil to a soluble product, particularly when high levels (i.e., >10% sulfur) are used. The sulfurization problem is due to cross-linking. For example, when triglyceride meadowfoam oil is sulfurized for two hours at 180°C, using 20 weight percent of sulfur using standard procedures, the resulting product is incompletely soluble in a hydrocarbon oil. This result is consistent with published observations of sulfurizing triglyceride meadowfoam oil (see Kammann et al. *supra*).

Rapeseed oil comes from *Brassica napus* and typically has a fatty acid composition of:

18:1	13%
18:2	11%
18:3	5%
20:1	10%
22:1	55%
Other	6%

Crambe abyssinica (crambe oil) is native to Mediterranean countries and typically has a fatty acid composition of:

18:1	17%
18:2	9%
18:3	6%
20:1	5%
22:1	55%
Other	8%

The sulfurized vegetable oils of the present invention are completely soluble in hydrocarbon and comprise from about 25% to about 75% of the vegetable oil in the triglyceride form and from about 75% to about 25% of a wax ester, wherein the wax ester is jojoba oil or is derived from a C₁₈-22 unsaturated acid and a C₁₈-22 unsaturated alcohol. Preferably, the wax ester is jojoba oil or a wax ester of meadowfoam oil, rapeseed oil or crambe oil. The combination of triglyceride vegetable oil such as meadowfoam oil and jojoba oil or a wax ester can be sulfurized at high sulfur concentrations, such as 20 weight percent of sulfur. The sulfurization concentrations are from about 10% to about 25% sulfur. Preferably, the sulfur concentration is from 12% to about 20%. For example, Table 1 illustrates the solubility and copper strip test results of sulfurized combinations of triglyceride meadowfoam oil and jojoba oil (as the wax ester).

TABLE 1

Sulfurized Combinations of Meadowfoam Oil and Jojoba Oil				
Run #	Oil (grams)	Sulfur (grams)	Solubility in 5% Mineral Oil	Copper Strip Test
1.	20 jojoba oil	4	soluble	2B
2.	20 meadowfoam oil	4	insoluble	-
3.	20 meadowfoam oil	3	hazy	3C
4.	15 jojoba oil + 5 meadowfoam oil	4	soluble	2A
5.	10 jojoba oil + 10 meadowfoam oil	4	soluble	2A
6.	5 jojoba oil + 15 meadowfoam oil	4	soluble	1B

The copper strip test is graded as follows: 1A, 1B, 2A and 2B are bright copper; 3A, 3B and 3C are stained copper; 4A and 4B are purple stained copper; and 5A and 5B are black copper.

A portion of the acid segment of meadowfoam oil has two double bonds present. When there are two double bonds in the same acid portion of the triglyceride molecule, as for example in meadowfoam oil or rapeseed oil or crambe oil, the result on sulfurization of the triglyceride at approximately 10% sulfur concentration is to produce a solid or very viscous product with limited solubility in hydrocarbon oils. Such a solid or very viscous product would not be an acceptable lubricant additive. The solid or very viscous product is formed due to cross-linking with sulfur and each other, such that some molecules may be produced which have large quantities of sulfur and small amounts of solubilizing ester or glyceride. The preferred wax ester for adding to triglyceride meadowfoam oil for sulfurizing, jojoba oil, has two double bonds in the same molecule but one double bond is in the acid portion of the molecule and the second double bond is in the alcohol portion of the molecule, far removed from the first double bond. Thus, jojoba oil behaves differently from meadowfoam oil, rapeseed oil or crambe oil.

Jojoba oil appears to be reacting with an intermediate to provide a solubilizing effect of the final product in hydrocarbon oils. A comparison of the sulfurized product of United States patent 3,986,966 with a saturated nonwax ester and the present invention with a wax ester (e.g., jojoba oil) and a triglyceride (rapeseed oil or meadowfoam oil) is as follows:

TABLE 2

C ₁₄₋₁₅ Alkyl Oleate		
	Table V of U. S. Patent No. 3,986,966	Jojoba Oil
Alcohol portion of ester	14-15 (saturated)	20-22 (unsaturated)
Fatty oil	Rapeseed	Meadowfoam
Ester/oil ratio	1.22:1	1.22:1
Sulfur, wt. %	9.5	17.7
Viscosity at 100° F SUS	2075	1189
Copper corrosion 3 hrs. at 212° F	1B	1A
Solubility	cloudy	clear

Despite the use of a molecule with two double bonds, the inventive combination for sulfurizing, provide a product with superior solubility characteristics in hydrocarbon oil.

Triglyceride meadowfoam oil can be converted to the wax ester form by a process of treating the triglyceride with LiAlH₄ or another reducing agent into meadowfoam alcohols, such as:



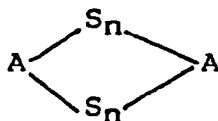
wherein n is 13 or 15 and glycerol is a by-product. The meadowfoam alcohols are added to the triglyceride meadowfoam oil in the presence of acid and heat to form more glycerol as a by-product and a meadowfoam wax ester:



wherein n is 13 or 15. Meadowfoam wax ester is structurally analogous to jojoba oil (except for the location of the double bonds) and is a mixture of long straight chain esters with 40 to 44 carbon atoms. As a structural analog to jojoba oil, meadowfoam wax esters have similar chemical properties to jojoba oil. Other vegetable oil triglycerides may be converted to the wax ester form by the same or similar processes. The resulting wax esters of rapeseed oil and crambe oil are chemically similar to the wax ester of meadowfoam oil.

Many sulfurized wax esters of vegetable oils may be used in combination with the lubricant additives of the present invention. A preferred sulfurized wax ester of a vegetable oil is the product of a reaction of the vegetable oil and 12% to 20% sulfur to yield the following:

A-Sn-A and

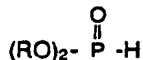


and mixtures of both,

wherein n is an integer from 1 to 3, and A refers to the vegetable wax ester.

For example, twenty grams of meadowfoam wax ester was sulfurized with 4 grams of sulfur at 180° C for 2 hours under nitrogen with stirring. The resulting sulfurized meadowfoam wax ester was soluble at a 5% concentration in mineral oil and had a 2B score in the copper strip test. Similarly, 20 grams of meadowfoam wax ester sulfurized in the same conditions with 3 grams of sulfur was soluble at a 5% concentration in mineral oil and had a 2A score in the copper strip test.

The phosphite adduct of the vegetable oil is formed by the reaction of triglyceride vegetable oil or a wax ester of a vegetable oil and a compound of the formula:



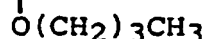
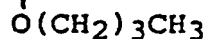
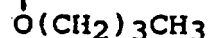
wherein R is H, C₁₋₁₂ alkyl, C₁₋₁₂ aryl, C₁₋₁₂ alkaryl, C₁₋₁₂ aralkyl, and cyclo C₁₋₁₂ alkyl. Preferably, R is C₄₋₈ alkyl, C₄₋₈ alkaryl, C₄₋₈ aralkyl, or cyclo C₄₋₈ alkyl. Most preferably, R is n-butyl.

As may be seen from the structural formulae, vegetable oil wax esters of the present invention have either two, three, or four carbon-carbon double bonds. Accordingly, the phosphite adduct of the wax ester of the vegetable oil can be either a di-adduct, a tri-adduct, or a tetra-adduct of the wax ester of the vegetable

oil.

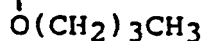
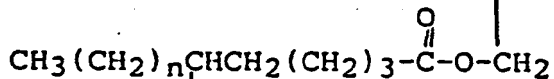
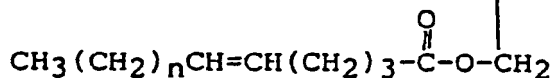
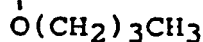
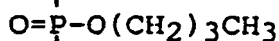
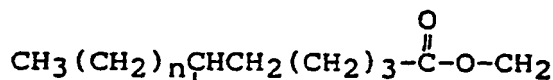
The triglyceride form of native vegetable oil can have between three and six carbon-carbon double bonds within the three fatty acids on the glycerol backbone. In extremely rare instances, there could be as many as nine double bonds. Therefore, depending upon the amount of phosphite added as a reactant for the triglyceride vegetable oil, the phosphite adduct of triglyceride vegetable oil can be a mono-, di-, tri-, tetra-, penta-, or a hexa-adduct. The penta-adduct should be a rare species and the hexa-adduct an extremely rare species according to Poisson distribution probabilities, because the frequency of dienes among the preferred vegetable oil fatty acids (i.e., meadowfoam, rapeseed, and crambe oils) is only approximately 20%. Thus, the tri-adduct should be the most common species. The preferred products are the mono-, di-, and tri-adducts.

The following are examples of species of the phosphite adduct of meadowfoam oil wax ester:

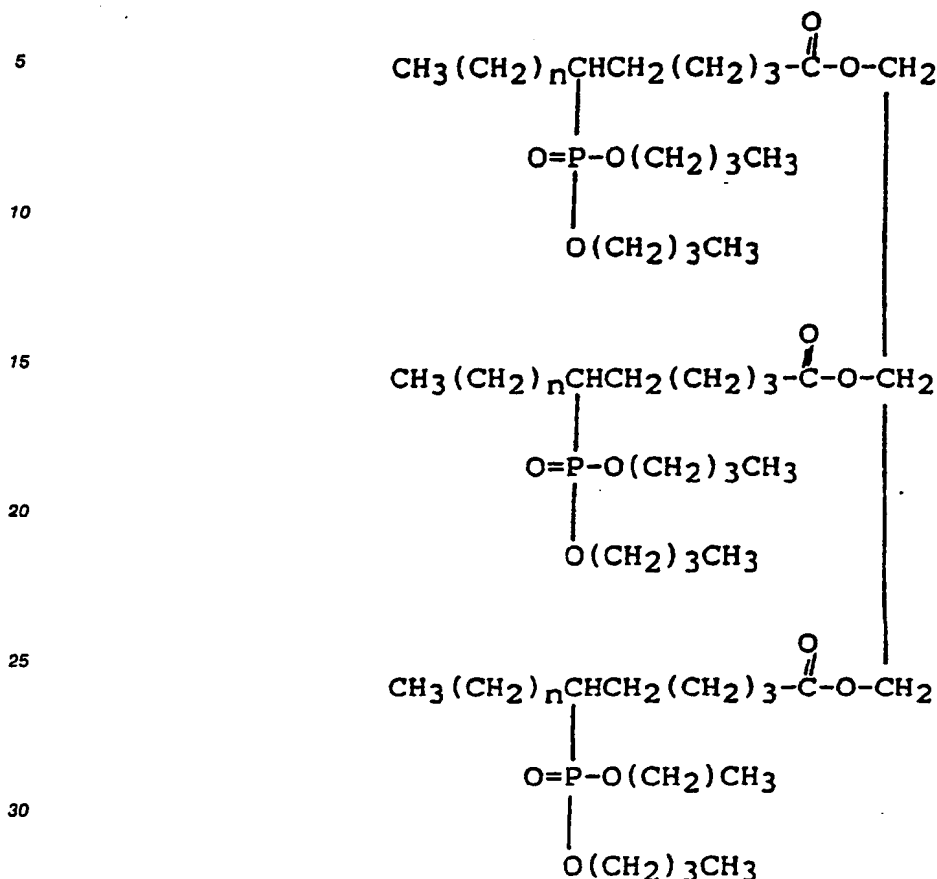


wherein n is 13 or 15.

The following are examples of species of the phosphite adduct of meadowfoam oil triglyceride:



and



wherein n is 13 or 15.

The present invention further relates to lubricating compositions, containing a lubricant additive. Depending upon the application and the desired extent of antiwear protection, the total additive concentration will range from about 0.1% to about 25% by weight. The lubricant additive comprises a combination of a vegetable oil as the triglyceride or wax ester or a combination of both (but not necessarily from the same vegetable oil source), and at least one of a sulfurized vegetable oil, as described herein, and/or a phosphite adduct of a vegetable oil as either the wax ester or the triglyceride or a combination of both, as described herein. Preferably, the lubricant additive comprises meadowfoam, rapeseed or crambe oil as a triglyceride, meadowfoam oil triglyceride in combination with jojoba oil and sulfurized at about 20% sulfur, and the phosphite adduct of meadowfoam oil triglyceride. The inventive lubricant additive can substitute a phosphite adduct of jojoba oil as described in copending U.S. Patent Application Serial No. 088,186, filed August 21, 1987 and incorporated by reference herein.

Depending upon the application of the final lubricant product and the desired extent of antiwear protection desired, the total lubricant additive concentration will vary from about 0.1% to about 25% by weight. For example, a lubricant additive may contain about 0.1% to about 5.0% of a triglyceride vegetable oil, a wax ester vegetable oil or a combination of both; about 0.2% to about 10.0% of sulfurized vegetable oil as defined herein; and from about 0.1% to about 5.0% of the phosphite adduct of a vegetable oil as defined herein. Preferably, the phosphite adduct of the vegetable oil is a monoadduct of dibutylphosphite of triglyceride vegetable oil.

Different combinations and concentrations of the lubricant additive components will depend upon the desired product attributes. For example, a hydraulic oil would have a lubricant additive comprising (percentages are by weight of total product) a relatively low concentration of the sulfurized vegetable oil (as defined herein) of about 0.1% to about 0.5%, a relatively high concentration of the triglyceride vegetable oil (approximately 2%) and a relatively low concentration of the phosphite adduct of the vegetable oil (as

defined herein) of approximately 0.5%. A metal cutting oil, for example, would have a lubricant additive comprising (percentages are by weight of total product) approximately 7% sulfurized triglyceride oil (as defined herein), and approximately 2% of the triglyceride vegetable oil and optionally approximately 0.5% of a phosphite adduct of the vegetable oil (as defined herein). An automotive engine oil, for example, would contain a lubricant additive comprising (percentages are by weight of total product) approximately 1% sulfurized vegetable oil (as defined herein) approximately 2% of the triglyceride vegetable oil, approximately 0.5% of the phosphite adduct of the triglyceride vegetable oil (as defined herein) and other additives as are normally used in an automotive engine oil.

The following example illustrates test model performance results from standard test including the 4-Ball Wear Test and the Falex Wear Test. The 4-Ball Wear Test assesses extreme pressure properties of the lubricant. The measurement of friction as related to rolling, drawing, and other metal-working operations depends upon the surface of the tool and workpiece and the viscosity and chemical makeup of the lubricant, as well as the pressure and temperature developed during processing. The 4-Ball wear test machine provides, under controlled testing conditions, a procedure for measuring friction. The machine consists of three balls touching each other and clamped together in a horizontal plane. A fourth ball touches three clamped balls by being positioned between the three and is driven by a motor so that it revolves in contact with the clamped balls. The rotation takes place within a reservoir containing a test lubricant. A temperature-measuring device, as well as a heater, provides a method for controlling the temperature of the test fluid. The rotating ball is loaded and then rotated for a specific time at a specific speed. At the conclusion of the test, the scar patterns developed on the balls are measured. Any stains are observed, the diameter of the scar is measured, and the coefficient of friction is calculated by dividing the tangential force by the normal force at the ball surface.

The Falex test consists of a method for measuring the torque and friction developed during rotation of a pin between two stationary V blocks. The pin as well as the V blocks can be made of various materials. The temperature of the lubricant bath into which the pin and V block are placed may also be varied. The load is applied by a ratchet arrangement. Wear measurements made above the transition pressure, that is, the load at which the lubricant film breaks down, can be a useful parameter if carried out under conditions comparable to actual operations.

The following examples are offered for illustration purposes and not by way of limitation.

EXAMPLE 1

This example illustrates 4-Ball and Falex Wear Test results for a 100 SUS solvent paraffinic mineral oil base fluid without a lubricant additive and with different lubricant additives as indicated. This example compares the model test system properties of lubricant additives composed of one component as compared with lubricant additives composed of two or three components.

TABLE 3

Lubricant	4-Ball Wear Scar Dia.(mm)	Wear Load (lbs)	Falex lbs to Failure
Base fluid	0.94	120	725
Base fluid + 1% meadowfoam oil	0.82	150	2600
Base fluid + 2% sulfurized meadowfoam oil ^a	0.55	210	4200
Base fluid + 1% meadowfoam phosphite adduct ^b	0.55	210	4200
Base fluid + 2% sulfurized meadowfoam oil ^a + 0.5% meadowfoam phosphite adduct ^b	0.42	280	4500
Base fluid + 1% meadowfoam oil + 1% sulfurized meadowfoam oil ^a + 0.5% meadowfoam phosphite adduct ^b	0.42	280	4500
Base fluid + 1% meadowfoam oil + 0.5% meadowfoam phosphite adduct	0.50	250	4000

^a The sulfurized meadowfoam oil is a mixture of 10 grams of triglyceride meadowfoam oil and 10 grams of jojoba oil sulfurized with 4 grams of sulfur (Run #5 in Table 1).

^b The meadowfoam phosphite adduct is a monoadduct of dibutyl phosphite with triglyceride meadowfoam oil.

EXAMPLE 2

This example illustrates a series of sulfurization experiments to determine whether various vegetable oils can be sulfurized on the basis of their oil-solubility and copper strip test results. In each experiment, 20 grams of oil were stirred and heated at 180°-200° C. Four grams of resublimed sulfur was added over a period of 20 minutes. Heating and stirring under a nitrogen atmosphere was continued for 2 1/2 hours. The oil-solubility at 5 weight % was determined by dissolving the sulfurized product by heating in mineral oil at 70° C with constant stirring and then allowing the mixture to cool at room temperature. The copper strip test was conducted at 30 minutes at 100° C and at 1 hour at 100° C. Test results showing a bright strip or a trace stain indicate an acceptable product. Unacceptable results include stains or coatings on the copper strip. Products that were insoluble in mineral oil were not able to be tested in a copper strip test. The results are indicated in Table 4 below.

TABLE 4

Product	Oil Sol.	Copper Strip Test	
	5 Wt. %	0.5 hr.@100°C	1 Hr. 100°C
Sulfurized Olive Oil	Mod. Haze	Bright	Trace Stain
Sulfurized Corn Oil	Heavy Haze	Lt. Stain	Purple Stain
Sulfurized Peanut Oil	Mod. Haze	Bright	Dk. Brn. Stain
Sulf. Safflower Oil	Mod. Haze	Bright	Mod. Stain

	Sulf. Cottonseed Oil	Heavy Haze	Bright	Bright
	Sulf. Cod Liver Oil	Insol.	-	-
5	Sulf. Jojoba Oil	Soluble	Bright	Bright
	Sulf. Meadowfoam Oil	Insol.	-	-
	Sulf. Rape Seed Oil	Insol.	-	-
	Sulf. Rapeseed Oil-			
10	Jojoba Oil (1:1)	Soluble	Bright	Bright
	Sulf. Agro Liq. Wax ¹	Soluble	Bright	Bright
	Sulf Rapeseed Oil-			
15	Jojoba Oil (3:1)	Mod. Haze	Dk. Coating	Dk. Coating
	Sulf. Corn Oil-			
	Jojoba Oil (1:1)	Soluble	Bright	Bright
	Sulf. Olive Oil-			
20	Jojoba Oil ((1:1)	Soluble	Bright	Trace Stain
	Sul. Peanut Oil-			
	Jojoba Oil (1:1)	Soluble	Bright	Bright
25	Sulf. Rapeseed Oil-			
	Jojoba Oil (1:3)	Soluble	Bright	Trace Stain
	Sulf. Corn Oil-			
30	Jojoba Oil (1:3)	Soluble	Bright	Bright
	Sulf. Crambe Oil	Insol.	-	-
	Sulf. Crambe Oil-			
	Jojoba Oil	Soluble	Bright	Bright
35	Sulf. Meadowfoam Oil-			
	Jojoba Oil (1:1)	Soluble	Bright	Bright
	Sulf. Meadowfoam Oil-			
40	Jojoba Oil (1:3)	Soluble	Bright	Bright
	Sulf. Meadowfoam Oil-			
	Jojoba Oil (3:1)	Sl. Sol.	Bright	Trace Stain

(1) Agro Liquid Wax is an analog of jojoba oil, i.e., it is a long chain monoester of rapeseed acids reacted with rapeseed oil alcohols.

Accordingly, the results in table 4 indicate that cosulfurization of vegetable oil improves the sulfurized oil's solubility and copper strip test results.

EXAMPLE 3

This example illustrates that the phosphite adduct of both triglyceride vegetable oil and the wax ester of vegetable oil can be phosphorylated and still results in a soluble product. In each case, the vegetable or

plant oil at a concentration of 0.01 mole was mixed with dibutyl hydrogen phosphite (0.01 mole) and di-
 butyl peroxide (0.02 gram). The mixture was heated and stirred at 155° C-165° C for three hours. At the end
 of three hours, the mixture was cooled under a blanket of nitrogen to remove traces of t-butanol. Solubility
 was determined at a 5% concentration in mineral oil. As shown in Table 5 below, the triglyceride oils, corn
 oil, peanut oil, cottonseed oil, rapeseed oil, crambe oil, meadowfoam oil and code liver oil were soluble.
 Additionally, the wax esters jojoba oil, rapeseed liquid wax ester and meadowfoam liquid wax ester were
 also soluble.

TABLE 5

Product	Solubility in Mineral Oil at 5 Wt. % Conc.
Jojoba Oil-DBHP Adduct	Soluble
Corn Oil-DBHP Adduct	Soluble
Peanut Oil-DBHP Adduct	Soluble
Cottonseed Oil-DBHP Adduct	Soluble
Cod Liver Oil-DBHP Adduct	Soluble
Rapeseed Oil-DBHP Adduct	Soluble
Crambe Oil-DBHP Adduct	Soluble
Agro Liquid Wax-DBHP Adduct	Soluble
Meadowfoam Oil-DBHP Adduct	Soluble
Meadowfoam meadowfoamate Liquid Wax ¹ -DBHP Adduct	Soluble

(1) Meadowfoam meadowfoamate Liquid Wax is an analog of jojoba oil, i.e., it is a long
 chain monoester of meadowfoam oil acids reacted with meadowfoam oil alcohols.

The principles, preferred embodiments, and modes of operation of the invention have been described in
 the foregoing specification. The invention which is intended to be protected herein, however, is not to be
 constrained as limited to the particular forms disclosed, since these are to be regarded as illustrative rather
 than restrictive. Variations and changes may be made by those skilled in this art without departing from the
 spirit and scope of the invention.

The features disclosed in the foregoing description, in the following claims and/or in the accompanying
 drawings may, both separately and in any combination thereof, be material for realising the invention in
 diverse forms thereof.

Claims

1. A lubricating composition consisting essentially of a lubricant base and a lubricant additive wherein
 the lubricant additive comprises a mixture of at least two ingredients from different classes of ingredients
 selected from the group consisting of three classes of ingredients:
 wherein the first class of ingredients comprises a triglyceride vegetable oil, a wax ester of a vegetable oil, or
 a combination thereof;
 wherein the second class of ingredients comprises a sulfurized vegetable oil wax ester, a sulfurized
 triglyceride vegetable oil comprising from about 25% to about 75% triglyceride vegetable oil, and from
 about 25% to about 75% of a wax ester, wherein said wax ester is derived from a C₁₈₋₂₂ unsaturated acid
 and a C₁₈₋₂₂ unsaturated alcohol or said wax ester is jojoba oil, or a combination thereof; and
 wherein the third class of ingredients comprises a phosphite adduct of triglyceride vegetable oil, a
 phosphite adduct of vegetable oil wax ester, or a combination thereof, with the proviso that at least 90% of
 the fatty acids of the vegetable oil are from about 16 to about 26 carbon atoms long and have at least one
 and no more than three double bonds.
2. A lubricant additive comprising a mixture of at least two ingredients from different classes of
 ingredients selected from the group consisting of three classes of ingredients:
 wherein the first class of ingredients comprises a triglyceride vegetable oil, a wax ester of the vegetable oil,
 or a combination thereof;
 wherein the second class of ingredients comprises a sulfurized vegetable oil wax ester, a sulfurized

triglyceride vegetable oil comprising from about 25% to about 75%, triglyceride vegetable oil and from about 25% to about 75% of a wax ester wherein said wax ester is derived from a C₁₈₋₂₂ unsaturated acid and a C₁₈₋₂₂ unsaturated alcohol or said wax ester is jojoba oil, or a combination thereof; and wherein the third class of ingredients comprises a phosphite adduct of triglyceride vegetable oil, a phosphite adduct of vegetable oil wax ester, a jojoba oil phosphite adduct, or a combination thereof, with the proviso that at least 90% of the fatty acids of the vegetable oil are from about 16 to about 26 carbon atoms long and have at least one and no more than three double bonds.

3. A lubricant additive comprising sulfurized triglyceride vegetable oil wherein from about 25% to about 75% triglyceride vegetable oil is sulfurized with from about 75% to about 25% of an unsaturated wax ester with at least two double bonds and from about 30 to about 60 carbon atoms straight chain length.

4. A lubricant additive comprising a phosphite adduct of a triglyceride vegetable oil is a mono-, di-, tri-, tetra-, penta- or hexa-adduct of the reaction product of (RO)₂- $\overset{\text{O}}{\underset{\text{O}}{\text{P}}}$ -H and triglyceride vegetable oil, wherein R is selected from the group consisting of H, C₁₋₁₂ alkyl, C₁₋₁₂ aryl, C₁₋₁₂ alkaryl, C₁₋₁₂ aralkyl, and cyclo C₄₋₁₂ alkyl.

5. A lubricant additive comprising sulfurized triglyceride vegetable oil, wherein said sulfurized triglyceride vegetable oil comprises the sulfurized product of from about 25% to about 75% triglyceride vegetable oil and from about 25% to about 75% of a wax ester, wherein said wax ester is derived from a C₁₈₋₂₂ unsaturated acid and a C₁₈₋₂₂ unsaturated alcohol, or said wax ester is jojoba oil.

6. The lubricating composition or lubricant additive of claims 1-5 wherein the vegetable oil is selected from the group consisting of meadowfoam oil, rapeseed oil, crambe oil and combinations thereof.

7. The lubricating composition of lubricant additive of claims 1 or 2 wherein the third class of ingredients is a mono-, di-, tri-, tetra-, penta- or hexa-adduct of the reaction product of

(RO)₂- $\overset{\text{O}}{\underset{\text{O}}{\text{P}}}$ -H and triglyceride vegetable oil or jojoba oil, wherein R is selected from the group consisting of H, C₁₋₁₂ alkyl, C₁₋₁₂ aryl, C₁₋₁₂ alkaryl, C₁₋₁₂ aralkyl, and cyclo C₄₋₁₂ alkyl.

8. The lubricating composition or lubricant additive of claims 4 or 7 wherein R is selected from the group consisting of C₄₋₈ alkyl, C₄₋₈ alkaryl, C₄₋₈ aralkyl, and cyclo C₄₋₈ alkyl.

9. The lubricating composition of claim 1 wherein the lubricant base is selected from the group of lubricant bases useful for an automobile engine oil, a precoat oil, a gear lubricant, a textile lubricant, an aviation oil, a grease, a hydraulic oil, a circulating oil, a diesel engine oil, an automatic transmission fluid, a way lubricant, a steam cylinder oil, a spindle oil, and a cutting fluid.

10. The lubricating additive or lubricating composition of claims 1, 2 or 4 wherein the phosphite adduct point of attachment to triglyceride vegetable oil, jojoba oil, or the wax ester of the vegetable oil is at a carbon-carbon double bond.

11. A process for sulfurizing a triglyceride vegetable oil, comprising: mixing from about 75% to about 25% of triglyceride vegetable oil with about 25% to about 75% of a wax ester of from about 30 to about 60 carbon atom straight chain length and at least two double bonds; and sulfurizing the mixture with from about 5% to about 25% sulfur by weight to form sulfurized triglyceride vegetable oil.

12. The process of claim 11 wherein the wax ester is selected from the group consisting of a wax ester of vegetable oil and jojoba oil.

13. The lubricant additive of claim 5 wherein said sulfurized triglyceride vegetable oil comprises about 50% triglyceride vegetable oil and about 50% vegetable oil wax ester.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A- 557 756 (WAKEFIELD & CO. LTD) * Page 2, lines 26-61; page 2, line 111 - page 3, line 5 *	1,2,6,9	C 10 M 159/02 C 10 M 135/06 C 10 M 163/00 //
Y	WO-A-8 606 371 (LUBRIZOL CORP.) * Page 6, line 29 - page 7, line 26; page 8, lines 14-34; page 10, lines 9-34; page 18, lines 8-24 *	3,5,11- 13	(C 10 M 163/00 C 10 M 135:06 C 10 M 159:02)
Y	US-A-4 152 278 (E.W. BELL) * Column 2, line 39 - column 3, line 32; column 9, lines 12-32 *	3,5,11- 13	C 10 N 30:06 C 10 N 60:10 C 10 N 60:12
D,P X	EP-A-0 308 651 (INTERNATIONAL LUBRICANTS) * Page 2, lines 45-55; page 4, lines 32-56; page 6, lines 35-45 *	1,2,7- 10	
D,A	CHEMICAL ABSTRACTS, vol. 102, no. 26, July 1985, page 131, abstract no. 222989t, Columbus, Ohio, US; K.P. KAMMANN Jr. et al.: "Sulfurized vegetable oil products as lubricant additives", & J. AM. OIL CHEM. SOC. 1985, 62(5), 917-23 * Abstract *	1-3,5,6 ,11,13	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 10 M
D,A	US-A-3 740 333 (R.B. HUTCHINSON) * Claims 1-4; column 3, lines 50-56; column 4, lines 20-27 *	1-3,5,6 ,9,11, 13	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-09-1989	Examiner HILGENGA K.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

